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Vol. 30. No. 248. August 1944.

THE APPLICATION OF FREE ENERGY EQUATIONS TO THE STUDY OF THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN.*

By W. W. Myddleton, D.Sc., F.R.I.C., F.Inst.Pet.

Synopsis.

Equations have been derived relating free energy of reaction to temperature in the synthesis of a series of gaseous hydrocarbons from carbon monoxide and hydrogen.

In building up these equations molecular heat-temperature curves were drawn for each reactant and product and molecular heat-temperature equations were fitted over the range 25–250° C., existing equations being generally unsatisfactory for the temperature range covering synthesis. Some use has been made of molecular heat and entropy values calculated from statistical and spectroscopic data.

The suppression of reactions in which carbon dioxide is formed, in spite of free energy changes favourable to them, is attributed to special conditions prevailing at the catalyst surface.

The appearance of traces of ethylene amongst the products of synthesis instead of appreciable quantities predicted by the free energy relationships is accounted for by the incorporation of ethylene actually formed into the building up of hydrocarbon chains.

The possibility of increasing the yields of *iso*butane and *iso*butene is considered worthy of attention. The formation of aromatic hydrocarbons requires a special orientation of reactants on the surface of the catalyst, and the probability of the necessary conditions occurring is slight.

The Gaseous Hydrocarbons.

The symbols employed are in accordance with the Joint Report of the Chemical, Faraday, and Physical Societies, 1937.

The Free Energy Equations and Their Uses.

In a study of the thermal characteristics of a reaction such as $n\mathrm{CO} + (2n + 1)\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{(2n+2)} + n\mathrm{H_2O}$ the thermal data available may be assembled in the form

$$\Delta H_T = \Delta H_0 + \mathrm{A}T + \mathrm{B}T^2 + \mathrm{C}T^3 \quad . \quad . \quad . \quad . \quad (1)$$

where ΔH_T is the change in heat content during reaction at $T°$ K. and ΔH_0 may be regarded as the change in heat content in hypothetical reaction at absolute zero. A, B and C are constants for a reaction producing any one hydrocarbon.

The application of equation (1) gives information necessary for the provision of adequate means of controlling the temperature in an exothermic reaction. Its general usefulness can be extended by deriving from it an equation showing the change in free energy during the reaction.

* Received 17th February, 1942. Released by Censor May 1944.

We thus obtain a thermodynamical approach to a series of practically important questions such as the following :—

1. What operating conditions can most profitably be explored ?
2. Is any other product or any other type of reaction of the same order of thermodynamic probability as the main reaction we are considering ? When this is the case there is always a danger, to be explored and provided for, of some alteration in working conditions or in the form of catalyst suddenly provoking a disturbance and perhaps producing undesirable products.
3. Can the non-occurrence of equally probable reactions be accounted for by a different mechanism at the catalyst surface, such that the conditions necessary for its accomplishment cannot be fulfilled in the prevailing circumstances ? The answer to this question may serve to evaluate the risk of undesirable complications dealt with in the previous question.
4. Do thermodynamical considerations show that some of the more desirable products can be formed in larger proportion ?

Such questions as these will be discussed with reference to the gaseous hydrocarbons which normally accompany liquid and solid hydrocarbons during synthesis from carbon monoxide and hydrogen.

For the development of equation (1) the constants A, B and C are derived from molecular heat-temperature equations for all the substances involved in the reaction. For each reactant and product an equation is obtained in the form $C_p = a + bT + cT^2$. Then by algebraically summing the molecular heats of the products and subtracting the sum of the molecular heats of the reactants we obtain ΔC_p for the reaction.

Substituting in the equation $\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$ and integrating we obtain A, B and C in equation (1). The integration constant ΔH_0 is evaluated by finding the value of ΔH_T for some fixed temperature in the range for which the molecular heat equations are valid. This is readily done by employing the data on heats of combustion of the substances involved in the reaction.

Substitution from equation (1) in the thermodynamical equation $\mathrm{d}\frac{\Delta G}{T} / \mathrm{d}T = -\frac{\Delta H}{T^2}$ followed by integration gives us the final free energy equation

$$\Delta G^\circ_T = \Delta H_0 + A'T \ln T + B'T^2 + C'T^3 + \ldots + IT \quad . \quad (2)$$

The integration constant I can be evaluated in relatively few ways. The value of ΔG°_T must be found for some fixed temperature in the specified range. For this purpose the equation $\Delta G^\circ_T = -RT \ln K$ is not generally applicable to the reactions we are considering because the equilibrium constant K is not often available. The most useful procedure is to apply the relation $\Delta G_T = \Delta H^\circ_T - T\Delta S^\circ_T$ at $T = 298{\cdot}1^\circ$ K., where ΔS°_T is the sum of the molecular entropies of the products at 298·1° K. less the sum of the molecular entropies of the reactants.

Previous thermodynamical treatment of the subject [1] has been marred by one or more of the following factors :—

A. Inaccurate thermal data such as heat of combustion, molecular heat at constant pressure, and entropy.

B. Lack of information on rates of reaction.

C. Lack of information on the difference between free energy change as normally calculated for conditions in which each reactant and each product is at atmospheric pressure, and, under the actual conditions of synthesis, when partial pressures are far removed from atmospheric.

These difficulties have been considered in the order given.

A.1. The Heat of Combustion of Reactants and Hydrocarbon Products.

In recent years highly accurate data on heats of combustion have been provided by Rossini, Jessup and their co-workers.

A.2. Molecular Heat at Constant Pressure.

We are concerned with the conditions in the catalyst space, and molecular heat values should therefore refer to gases and vapours. When we examine recorded experimental figures, we find very serious discrepancies, even in the case of such gases as the oxides of carbon. A critical study of the methods employed in the observations reveals that, where possible sources of error have been reduced and when special refinements in apparatus or technique have been introduced, the values obtained are in good agreement with those calculated from the characteristic vibration frequencies of the molecules by the application of the Planck–Einstein equation.[2]

For such gases molecular heats have been calculated from what are considered to be the most reliable vibration frequencies recorded in the literature.

Calculation is as yet unsatisfactory in the case of the more complex gases. Not all of the characteristic frequencies of a complex molecule can be derived from the infra-red and Raman spectra, the usual source of such information, and, in fact, experimental specific heat values have been employed to predict missing frequencies in ethylene [3] and ethane.[4] Another kind of difficulty is found in ethane and in general in molecules containing a C-C bond. There is undoubted evidence of a restriction in the freedom of rotation about this bond, and until its magnitude has been ascertained we cannot calculate the molecular heat due to the internal rotations of the molecule.[4, 5]

For hydrocarbon gases other than methane, therefore, the best experimental values have been selected from the literature.

Method of Calculation.

The contribution made to the molecular heat at constant volume by

each mode of vibration of the molecule was found by applying the Planck–Einstein equation in the form

$$C_{vib} = R\left[\frac{e^{\frac{\theta}{T}}\left(\frac{\theta}{T}\right)^2}{\left(e^{\frac{\theta}{T}}-1\right)^2}\right] \times (\text{Degrees of freedom})$$

where R is the molecular gas constant, taken here as 1·9863 cal.; e is the base of natural logarithms; θ is the characteristic temperature of the vibration = 1·4327 × (Number of wave-lengths per centimetre).

The selection of characteristic frequencies from the spectra and the assignment to them of their appropriate degrees of freedom has become a highly specialized branch of science. An extensive examination of the data recorded in the literature has been made.

The total molecular heat at constant volume was obtained by adding the effects due to translation, rotation and vibration.

Type of molecule.	$C_v = C_{trans.} + C_{rot.} + C_{vib.}$
Diatomic.	$C_v = \frac{3}{2}R + R + C_{vib.}$
Triatomic linear.	
CO_2 type.	$C_v = \frac{3}{2}R + R + C_{vib.}$
Triatomic non-linear.	
H_2O type.	$C_v = \frac{3}{2}R + \frac{3}{2}R + C_{vib.}$
Polyatomic. CH_4 type.	$C_v = \frac{3}{2}R + \frac{3}{2}R + C_{vib.}$

Calculation of C_p at atmospheric pressure.

Conversion of C_v to C_p at infinite dilution was obtained from the equation $C_p = C_v + R$.

The correction for increase in pressure to 1 atmosphere was made in the usual manner by assuming that the gas obeys Berthelot's equation of state. Then if P_c and T_c are the critical pressure and temperature

$$C_{p-1} = C_{p-0} + R\left[1 + \frac{81}{32} \times \frac{1}{P_c} \times \left(\frac{T_c}{T}\right)^3\right].$$

A.3. Molecular Heat Equations.

Many of the molecular heat equations in common use are constructed for temperatures beyond the range in which we are interested. New equations have therefore been obtained fitting the graphs molecular heat–absolute temperature for each gas over the range 25° to 250° C.

A.4. Evaluation of the Integration Constant ΔH_0.

The value of the integration constant ΔH_0 in the free energy equation (2) can be found from equation (1) when we find ΔH_T at some definite temperature within the specified range for which the molecular heat equations have been constructed.

Heats of combustion afford the means of doing this, and as they are usually reported for 298·1° K., this temperature is used for determining ΔH_T. Reported values account for any water formed in the liquid state.

We must therefore take into account the latent heat of vaporization of water at 298·1° K.

A.5. Molecular Entropy.

The experimental determination of entropy involves the measurement of specific heat down to temperatures preferably below 10° K., and thereafter a graphical extrapolation to absolute zero. The method of extrapolation has been simplified by Kelley, Parks and Huffman.[6] The latent heat appropriate to any change in state or form between absolute zero and 298·1° K. must be measured and used in the calculation.

The difficult procedures in the determination make it desirable to compare experimental values with those calculated for the simpler types of gas from statistical and spectroscopic data.

Important discrepancies between the two sets of values in the cases of carbon monoxide, water vapour and hydrogen require investigation before we decide to adopt any particular figure.

Entropy of Carbon Monoxide.

If the assumption is made that the molecule behaves as though it were unsymmetrical in the crystalline solid, the entropy due to rotation is 11·375 entropy units, and the total entropy of the gas at 298·1° K. is 47·298 E.U. The experimental value reported by Clayton and Giauque [7] is 46·22 E.U.

There is some independent experimental evidence that the molecule behaves as though it were symmetrical. If this were the case, the rotational entropy would be 9·998 E.U. and the total entropy at 298·1° K. would be 45·92 E.U. The value taken for the calculation of free energy is the mean value of 46·07 E.U.

Entropy of Water Vapour.

The calculated value is $S^\circ_{298\cdot1} = 45\cdot09$ E.U. Direct experimental methods according to Giauque and Stout [8] gave $S^\circ_{298\cdot1} = 44\cdot28$ E.U. A suspicion of randomness in the ice crystals led to an indirect method in which Giauque and Archibald [9] studied the reaction $Mg(OH)^2 = MgO + H_2O$. This method gave $S^\circ_{298\cdot1} = 45\cdot10$ E.U.

Entropy of Hydrogen.

The experimental determination by Giauque [10] gave $S^\circ_{298\cdot1} = 29\cdot69$ E.U. From statistical and spectroscopic data Giauque [11] calculated $S^\circ_{298\cdot1} = 31\cdot23$ E.U. The discrepancy has been accounted for by Moelwyn Hughes [12] as being due to a difference between the entropies of *ortho-* and *para-*hydrogen. The entropy of the equilibrium mixture is calculated to be 29·59 E.U. from statistical and spectroscopic data.

The evidence at first sight appears to favour the adoption of the lower figure. It is, however, improbable that the same equilibrium mixture is concerned in synthesis. Furthermore, we can derive a value for the entropy of hydrogen from the free energy of the reaction $H_2 + \frac{1}{2}O_2 = H_2O$ for which four different methods give $\Delta G^\circ_{298\cdot1} = -54{,}507$ cal. as an average.[13] Assuming for water vapour $S^\circ_{298\cdot1} = 45\cdot10$ E.U. and for oxygen $S^\circ_{298\cdot1} = 49\cdot07$ E.U. we derive for hydrogen $S^\circ_{298\cdot1} = 31\cdot79$ E.U.

The conditions under which the free energy of formation of water was determined appear to exclude the possibility of normal equilibrium mixture of *ortho-* and *para*-hydrogen being involved.

The value 31·23 E.U. has been adopted.

The entropies of gases are usually referred to standard conditions at 298·1° K. and 1 atmosphere pressure and, furthermore, the gas is assumed to be in the ideal state in which the fugacity is also 1 atmosphere. When the gas is not ideal a correction can be applied by assuming, for example, Berthelot's equation of state. A gas obeying this law has an entropy lower than that of an ideal gas [14] by $\boldsymbol{R}\frac{27P}{32P_c}\left(\frac{T_c}{T}\right)^3$.

The correction is negligibly small for the gases and pressure and temperature conditions we are investigating.

For hydrocarbons other than methane the best experimental entropies have been adopted.

B. Rate of Reaction.

A method has been described for the measurement of the time of contact, and hence the rate of reaction under the conditions of gas flow of practical synthesis.[15] Observations will be given on the rate of formation of methane and carbon dioxide.

C. Correction to be Applied to Free Energy of Reaction for Differences in Pressure.

Free energy equations such as (2) are based upon the assumption that each gaseous product and reactant exerts a pressure of 1 atmosphere. We can estimate the approximate correction to be made for the actual conditions operating during synthesis.

For this purpose it has been assumed that blue water gas is used for synthesis and that 75 per cent. of the available carbon monoxide is converted into a single hydrocarbon at 200° C. and at a total pressure of 1 atmosphere. The partial pressures of reactants and products in the residual gas have been calculated for these conditions.

From the equation

$$G_x - G_1 = \int_1^x V\mathrm{d}P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the suffix 1 relates to the standard pressure of 1 atmosphere and x to the actual condition, we obtain

$$G_x - G_1 = \boldsymbol{R}T \ln \frac{P_x}{P_1}$$

and for the general reaction

$$n\mathrm{CO} + (2_{n+1})\mathrm{H}_2 = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O} \quad . \quad . \quad . \quad (4)$$

we have

$$G_x - G_1 = \boldsymbol{R}T \ln \frac{p(C_n\mathrm{H}_{2n+2}) \times p^n(\mathrm{H}_2\mathrm{O})}{p^n(\mathrm{CO}) \times p^{2n+1}(\mathrm{H}_2)} \quad . \quad . \quad . \quad (5)$$

For the conversion of 1 gram molecule of carbon monoxide in a reaction of this type the following values of $G_x - G_1$ have been calculated :—

Hydrocarbon formed.	Correction, calories.
Methane	2415
Ethane	2232
Propane	2255
Butanes	2264
Ethylene	2005
Propylene	2092
Butenes	2127

There is an alternative type of reaction in which carbon dioxide is formed instead of water.

$$2n\mathrm{CO} + (n+1)\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{CO_2} \quad . \quad . \quad . \quad (6)$$

For this type of reaction the corrections are :—

Hydrocarbon formed.	Correction, calories.
Methane	1413
Ethane	1093
Propane	1070
Butanes	1090
Butenes	1010

The gases have been assumed to obey the ideal gas laws, but the replacement of partial pressures by fugacities makes no significant alteration at the low pressures concerned.

Tables of Data Employed.

TABLE I.

Statistical and Spectroscopic Data.

Gas.	θ.	Degree of freedom.	Reference.
Carbon monoxide . .	3080	1	16
Hydrogen . . .	6017	1	17
Carbon dioxide . .	956	2	18
	1914	1	
	3367	1	
Water vapour . . .	2286	1	19
	5158	1	
	5382	1	
Methane	1870	3	20
	2182	2	
	4182	1	
	4311	3	

TABLE II.

Molecular Heat at Constant Pressure, 1 atm.

Constants for equation $C_p = a + bT + cT^2 + dT^3$.

Gas.	a.	$b \times 10^3$.	$c \times 10^6$.	$d \times 10^9$.	Refs. for expt. values used.
Carbon monoxide	6·936	− 0·01	− 0·08	+1·625	—
Hydrogen *	6·956	+ 0·07	—	—	—
Carbon dioxide	5·79	+11·0	− 2·0	—	—
Water vapour †	9·197	− 5·3	+ 6·36	+3·0	—
Methane †	4·50	+13·3	—	—	—
Ethane	3·80	+30·0	—	—	21
Propane	8·512	+31·375	—	—	22
Butane (*n*)	10·89	+40·0	+ 2·0	—	23
Butane (*iso*)	11·95	+30·0	+20·0	—	23
Ethylene	3·9	+22·0	—	—	21
Propylene	3·972	+37·23	—	—	23
Butene (1)	4·61	+51·3	—	—	23
Butene (*iso*) assumed	4·61	+51·3	—	—	—

* In calculating the molecular heat of hydrogen the correcting term $0{\cdot}000{,}08T$ was added.[24]

† Wilson [25] has shown that correction should be made here for distortion of the molecule by adding $2\rho RT$. For water $\rho = 2{\cdot}04 \times 10^{-5}$ and for methane $\rho = 1{\cdot}72 \times 10^{-5}$. The corrections have been applied.

TABLE III.

Standard Molecular Entropy at 298·1° K.

Gas.	$S^\circ_{298\cdot1}$ obs.	Refs.	$S^\circ_{298\cdot1}$ calc.	Refs.	$S^\circ_{298\cdot1}$ adopted.
Carbon monoxide	46·22 E.U.	7	45·92 E.U. 47·30 *	—	46·07 E.U.
Hydrogen	29·69	10	31·23 29·59 †	11 12	31·23
Carbon dioxide	51·11	26	50·83 51·07 ‡	— 27	51·00
Water vapour	45·10 44·28	9 8	45·09	—	45·10
Methane §	43·95 43·39 44·60 44·34	28 29 30	44·46 44·64 44·35	31 32 33	44·48
Ethane	54·85	34	—	—	54·85
Propane	64·70	35	—	—	64·70
Butane (*n*)	75·80	36	—	—	75·80
Butane (*iso*)	70·00				70·00
Ethylene	52·48	37	—	—	52·48
Propylene	63·10	38	—	—	63·10
Butene (1)	72·50	39	—	—	72·50
Butene (*iso*)	69·00				69·00

* Assuming molecule asymmetric in solid.

† Corrected for equilibrium mixture *ortho* and *para* forms.

‡ Different moment of inertia taken. More accurate method of calculation employed.

§ The first two experimental values quoted contained integration of Eastman's equation for molecular heat of methane. This equation is not accurate for the temperature range. Correction of second value gives the fourth value.

TABLE IV.

Heat of Combustion Employed, 298·1° K., 1 atmos.

Gas.	Heat of combustion, g. cal. per g. mol	Refs.
Carbon monoxide . . .	67,636	40
Hydrogen (H_2O liq.) . . .	68,318	41
Hydrogen (H_2O vap.) . . .	57,877 *	42
Methane (H_2O liq.) . . .	212,790	43
Ethane (H_2O liq.) . . .	372,810	44
Propane (H_2O liq.) . . .	530,570	45
Butane (*n*) (H_2O liq.) . .	687,940	44
Butane (*iso*) (H_2O liq.) . .	686,310	45
Ethylene (H_2O liq.) . . .	337,280	46
Propylene (H_2O liq.) . . .	491,820	46
Butene (1) (H_2O liq.) . . .	649,660	46
Butene (*iso*) (H_2O liq.) . .	647,200	41

* From latent heat of vaporization.

The latent heat of vaporization of water at 298·1° K. has been taken as 10,441 cal. per mol.[43]

TABLE V.

Free Energy Equations for Reactions of the Type

$$nCO + (2n + 1)H_2 = C_nH_{2n+2} + nH_2O \text{ (25–250° C.).}$$

General equation $\Delta G_T = \Delta H_0 + AT \ln T + BT^2 + CT^3 + DT^4 \ldots + IT.$

Hydrocarbon formed.	$\Delta H_0 \times 10^{-3}$.	A.	B × 10^3.	C × 10^6.	D × 10^{10}.	I.
Methane . .	− 45·560	14·107	− 3·90	−1·08	−1·2	−41·680
Ethane . .	− 76·249	26·458	− 9·54	−2·15	−2·3	−67·690
Propane . .	−110·13	33·397	− 7·51	−3·22	−3·4	−61·486
Butane (*n*) .	−144·05	42·671	− 9·11	−4·63	−4·6	−69·913
Butane (*iso*) .	−145·708	41·610	− 4·11	−7·63	−4·6	−59·081
Ethylene . .	− 45·212	19·402	− 5·57	−2·15	−2·3	−51·643
Propylene .	− 81·547	30·981	−10·47	−3·22	−3·4	−73·165
Butene (1) .	−114·702	41·994	−14·79	−4·30	−4·6	−90·010
Butene (*iso*) .	−117·162	41·994	−14·79	−4·30	−4·6	−86·510

TABLE VI.

Free Energy Equations for Reactions of the Type

$$2nCO + (n + 1)H_2 = C_nH_{2n+2} + nCO_2 \text{ (25–250° C.).}$$

Hydrocarbon formed.	$\Delta H_0 \times 10^{-3}$.	A.	B × 10^3.	C × 10^6.	D × 10^{10}.	I.
Methane . .	− 54·955	17·494	−12·09	+0·32	+ 2·7	− 50·950
Butane (*n*) .	−181·651	56·218	−41·87	+0·90	+11·0	−106·89

Relative Values of Terms Involving B, C and D.

For the equations in Tables V and VI terms in D contribute less than 0·1 per cent. to the total free energy. D and C terms together contribute less than 2 per cent. D, B and C together contribute less than 10 per cent.

TABLE VII.

Molecular Free Energy of Formation of Gaseous Hydrocarbons from Carbon Monoxide and Hydrogen.

A. Reaction in which water vapour is formed.
B. Reaction in which carbon dioxide is formed.

Hydrocarbon.	Reaction.	$G^{\circ}_{288\cdot1}$, g.-cal.	$G^{\circ}_{473\cdot1}$, g.-cal.	$G^{\circ}_{473\cdot1}$,* g.-cal.
Methane	*A*	− 34,401	−25,165	−25,165
Methane	*B*	− 41,495	−30,738	−15,369
Ethane	*A*	− 52,395	−33,540	−16,770
Propane	*A*	− 72,493	−43,938	−14,646
Butane (*n*)	*A*	− 93,355	−55,338	−13,834
Butane (*n*)	*B*	−121,730	−77,682	− 9,710
Butane (*iso*)	*A*	− 93,254	−54,373	−13,593
Ethylene	*A*	− 28,209	−14,595	− 7,298
Propylene	*A*	− 51,756	−28,582	− 9,527
Butene (1)	*A*	− 71,641	−38,699	− 9,675
Butene (*iso*)	*A*	− 73,059	−39,505	− 9,876

* Per g.mol. CO converted.

Discussion of Free Energy of Reaction.

The high negative values of the molecular-free energy of the reactions and the slope of the free energy *vs* temperature curve show that the lower limit of temperature will be determined by the rate of reaction. A more active form of catalyst would allow of lower working temperatures.

Formation of Carbon Dioxide.

The reaction in which carbon dioxide is formed has a higher negative free energy than the reaction producing water. It would therefore be expected to accompany the reaction in which water is formed. In the normal working of the synthetic process with nickel and cobalt catalysts the production of carbon dioxide is suppressed, but it can be initiated and allowed to replace the water-forming reaction by raising the temperature five to ten degrees above the optimum point. In the intermediate stages both carbon dioxide and water are produced, and methane appears in amount about equivalent to the carbon dioxide formed. With the entire suppression of water formation, methane is practically the only hydrocarbon to be made.

The elimination of the carbon dioxide reaction cannot be accounted for by a low rate of reaction. Aicher, Myddleton and Walker [15] have shown that on a nickel catalyst at about 180° C. the rate of conversion of carbon monoxide, present in water gas, into higher hydrocarbons and water is in the region of 20 normal litres per litre of catalyst space per hour.

A quantity of the same catalyst in an aluminium tube controlled at 180° C. by an electrically heated and controlled aluminium block produced methane and carbon dioxide from the time blue water-gas was admitted for an observed period of ten days. The flow of gas was maintained at the rate of approximately 100 litres per hour for a catalyst volume of 200 c.c. The inlet and outlet gases averaged :—

	Inlet, vol.-%.	Outlet, vol.-%.	From 100 vols. inlet.	
			Consumed, vols.	Produced, vols.
CO_2	2·9	36·5	—	18·9
Olefines	nil	0·2	—	—
CO	40·8	1·3	40·0	—
CH_4	2·4	36·7	—	19·5
H_2	48·4	15·4	39·2	—
N_2 (diff.)	5·5	9·9	—	—
	100·0	100·0		

The contraction in volume was 40·3 per cent.

One litre of catalyst space thus converted 200 litres of carbon monoxide per hour into methane and carbon dioxide.

The catalyst was found to contain about 0·5 per cent. free carbon after the reaction.

These facts point to different mechanisms in the two types of reaction. A similar conclusion was reached by Craxford [47] from a study of the rates of formation and reduction of cobalt carbide, assumed to be formed as an intermediate during synthesis with cobalt catalysts, by reaction of the metal with carbon monoxide and hydrogen.

$$\begin{matrix} & & O & & \\ & & \| & & \\ & & C & & \\ Co & - & Co & - & Co \end{matrix} + H_2 \longrightarrow \begin{matrix} & & C & & \\ & & / & & \\ Co & - & Co & - & Co \end{matrix} + H_2O$$

The formation of higher hydrocarbons and water is accounted for by reaction between the carbide and molecular hydrogen. The formation of methane is assumed to be due to reaction of the carbide with chemi-sorbed hydrogen, while carbon dioxide is produced by the process $CO + H_2O = CO_2 + H_2$. When higher hydrocarbons and water are formed, long-chain molecules are built up from methylene groups, the immediate reduction products of the carbide, and are broken down into lower-molecular-weight hydrocarbons by chemi-sorbed hydrogen.

On this basis the behaviour of iron catalysts is anomalous in many ways. When they form higher hydrocarbons they produce carbon dioxide simultaneously to the exclusion of water.[48] Furthermore, the hydrocarbons have a much higher average molecular weight than those formed on nickel and cobalt catalysts.

It appears possible to account for the behaviour of all three catalysts by assuming that when carbon monoxide is adsorbed by dual attachment at adjacent atoms on the catalytic surface, water is formed by subsequent reaction with molecular hydrogen. Methylene groups are formed at the same time, and give rise to hydrocarbon chains. When carbon monoxide is adsorbed by single attachment, molecular hydrogen produces methylene groups and carbon dioxide. The methylene groups may be converted into methane by the action of chemi-sorbed hydrogen.

The difference in spacing of the metallic atoms in iron catalysts may

account for absence of dual attachment of carbon monoxide in this case. Experimental evidence is being sought.

The view has been expressed by H. S. Taylor [49] that at 270° C. carbon monoxide attaches itself to nickel catalysts in the form of Ni_3C and NiO. For the purpose of the present discussion it is not necessary to assume that the bond energy between carbon and nickel is sufficiently high to give rise to carbide. The carbon would be more reactive if this were not the case.

Formation of Ethylene.

On purely thermodynamical grounds we should expect much more than the traces of ethylene normally produced. Typical figures obtained during the treatment of 3000 cu. ft. of blue water-gas per hour at approximately 200° C. are :—

$$\text{Carbon converted to ethylene} - - - \text{trace}$$

$$\text{Ratio } \frac{\text{Carbon to propylene}}{\text{Carbon to propane}} \; 1{\cdot}3$$

$$\text{Ratio } \frac{\text{Carbon to butene}}{\text{Carbon to butane}} \; 2{\cdot}2$$

The free energy values point to a decline in the ratio from C_4 to C_2 with an appreciable formation of ethylene. The difference in the rates of hydrogenation of propylene and ethylene is insufficient to explain the absence of ethylene. We therefore seek the explanation at the surface of the catalyst.

It was demonstrated by Smith, Hawk and Golden [50] that when ethylene is admitted along with carbon monoxide and hydrogen, a substantial part of it is used up in the formation of higher hydrocarbons. Twigg and Rideal [51] showed that ethylene is adsorbed on the surface of a nickel catalyst by dual attachment on adjacent nickel atoms in the 110 and 111 planes of the face-centred cubic crystals. Herington therefore accounts for the incorporation of ethylene in the synthesis of higher hydrocarbons by assuming that synthesis normally occurs on the same planes.[52]

Formation of Branched-chain Hydrocarbons.

The free energy relationships point to the formation of appreciable quantities of these hydrocarbons. Schaarschmidt and Marder [53] found 33 per cent. *iso*-paraffins in the paraffinic constituents of the synthetic gasoline fraction, and Koch and Hilberath [54] reported analyses showing presence of such compounds as 2-methyl butane, 2-methyl pentane, 3-methyl hexane, 3-methyl butene-1, 3-methyl pentene-1, 4-methyl pentene-1, 4-methyl hexene-1, and 5-methyl hexene-1. Little work has been carried out on the C_4 fraction.

As a preliminary to a systematic investigation of the C_4 fraction, samples were obtained by fractionation in a Podbielniak column. The light hydrocarbon fraction from which it was derived came from the treatment of blue water-gas on a cobalt catalyst. A C_4 sample was treated with 63 per cent. sulphuric acid according to the method of Dobryanskii.[55] The absorption, assumed due to *iso*butylene, was 14 and 16 per cent. in two

cases. According to the method of Frey and Yant,[56] in which absorption in a mixture of 2 vols. H_2SO_4 (sp. gr. 1·84) and 1 vol. water is measured, 16 and 19 per cent. *iso*butylene was found.

The possibility of formation of aromatic hydrocarbons during synthesis may be considered to require an orientation of molecules at the surface of the catalyst which is ruled out by the conditions prevailing, particularly when dual attachment of the carbon monoxide molecule is involved in the mechanism of synthesis. No such special orientation is required for the production of branched-chain hydrocarbons of the paraffin and olefine series.

In view of the importance of *iso*butane and *iso*butene as material for the production of motor spirit of high octane number and as material for chemical transformations for other purposes, a systematic investigation is planned to determine whether by modification of catalyst or in mode of operation the yield of these substances can be increased.

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FRACTIONAL DISTILLATION OF BINARY MIXTURES. SIMPLIFIED COMPUTATION OF THEORETICAL PLATES AND TRANSFER UNITS.

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Summary.

Equations, in convenient form for numerical computation, are derived for the number of theoretical plates or transfer units required for the separation of binary mixtures of normal volatility. When the top or bottom product contains only a small amount of one of the components, computation can be simplified by using certain approximate equations which give satisfactory accuracy. By a simple transformation a calculation for a stripping column can be converted into one for a rectifying column.

In a previous paper [1] equations were derived for the number of transfer units required for the fractionation of a binary mixture, in which the components follow Raoult's law and the relative volatility is constant. It was also shown there that these equations, as well as a modification of the equation published by Smoker [2] for the number of theoretical plates, can be used to convert any separation with finite reflux into an equivalent separation with total reflux. Computation of a numerical example is however rather laborious when using these equations either for transfer units or theoretical plates. This is particularly the case for separations in which the top or bottom product contains only a small amount of one of the components. It will be shown that equations can be derived which offer considerable advantage in these respects.

Number of Theoretical Plates

By making use of a property of the rectangular hyperbole, an equation for the number of theoretical plates can be derived quite simply. In Fig. 1 is shown part of a rectangular hyperbola, $y = \frac{Ax}{B + x}$, which passes through the origin 0 and has asymptotes $x = -B$ and $y = A$ parallel to the axes of co-ordinates. A line through the origin, $y = mx$, intersects the hyperbola again at L. A line parallel to OX intersects the hyperbola at P and the line OL at Q. The co-ordinates of P are (x_1, y_1) and those of Q are (x_0, y_1).

Then
$$mx_0 = y_1 = \frac{Ax_1}{B + x_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the abscissa of L is l, then

$$ml = \frac{Al}{B + l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Dividing equation (1) by equation (2),

$$\frac{x_0}{l} = \frac{x_1(B+l)}{l(B+x_1)}$$

and

$$\frac{x_0}{l-x_0} = \frac{x_1(B+l)}{B(l-x_1)}$$

and

$$\frac{\frac{x_0}{l-x_0}}{\frac{x_1}{l-x_1}} = \frac{B+l}{B} \quad \ldots\ldots\ldots \quad (3)$$

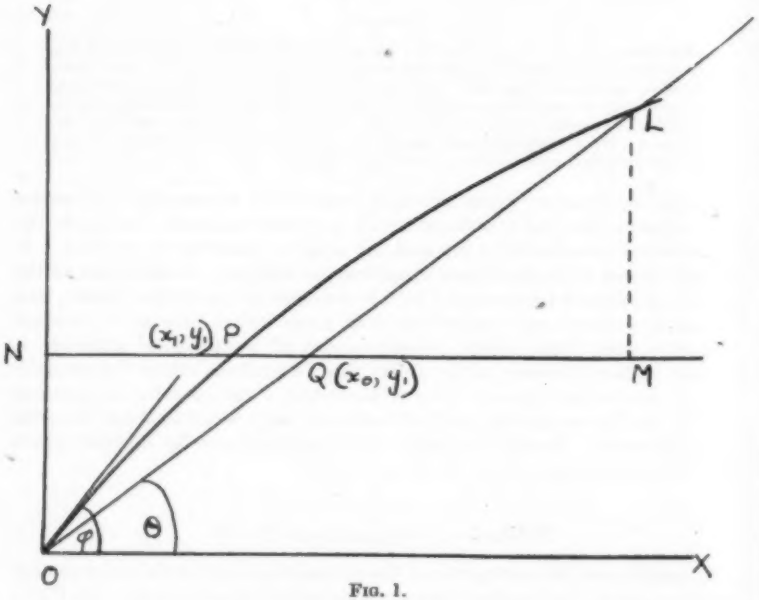

FIG. 1.

This ratio is therefore constant for any pair of points such as P and Q determined by any horizontal line such as NM. From equation (2),

$$\frac{B+l}{B} = \frac{A}{Bm}.$$

The slope of the tangent at a point on the hyperbola is given by

$$\frac{dy}{dx} = \frac{AB}{(B+x)^2} \quad \text{and} \quad \frac{dy}{dx} = \frac{A}{B}$$

when $x = 0$. The constant $\frac{A}{Bm}$ is therefore equal to $\frac{\tan\phi}{\tan\theta}$, where ϕ is the angle between the tangent to the hyperbola at 0 and the x axis and θ is the angle between the line OL and the x axis.

This is also evident from the following derivation:

$$\frac{\dfrac{x_0}{l-x_0}}{\dfrac{x_1}{l-x_1}} = \frac{y_1}{x_1} \cdot \frac{(l-x_1)}{(l-x_0)} \cdot \frac{x_1}{y_1}$$

As the line NM approaches the x axis and the points P and Q approach O, x_1 and x_0 become small and $\dfrac{l-x_1}{l-x_0}$ becomes unity in the limit. $\dfrac{y_1}{x_1}$ is the tangent of the angle between the line OP and the x axis. When P and O coincide, the line OP becomes the tangent to the hyperbola at O. $\dfrac{y_1}{x_0}$ is the tangent of the angle between OL and OX. As the ratio

$$\frac{\dfrac{x_0}{l-x_0}}{\dfrac{x_1}{l-x_1}}$$

is constant for any two points such as P and Q, it is equal to the value when P and Q coincide with O—*i.e.*, $\dfrac{\tan\phi}{\tan\theta}$.

Equation (3) may therefore be written:

$$\frac{\dfrac{x_0}{l-x_0}}{\dfrac{x_1}{l-x_1}} = \frac{\dfrac{NQ}{QM}}{\dfrac{NP}{PM}} = \frac{\tan\phi}{\tan\theta} \quad \ldots\ldots (4)$$

Fig. 2 shows the usual equilibrium curve $y = \dfrac{\alpha x}{1+(\alpha-1)x}$ (which is a rectangular hyperbola with asymptotes parallel to the axes) and an operating line $y = mx + b$ cutting the equilibrium curve at O' and L, the abscissæ of which are k_1 and k_2 respectively. P_0 and P are points representing the compositions on two adjacent plates with abscissæ x_0 and x_1 respectively. All co-ordinates now refer to the usual origin 0.

It has been shown that

$$\frac{\dfrac{NQ}{QM}}{\dfrac{NP}{PM}} = \frac{\tan\phi}{\tan\theta}$$

i.e.,

$$\frac{\dfrac{x_0-k_1}{k_2-x_0}}{\dfrac{x_1-k_1}{k_2-x_1}} = \frac{\tan\phi}{\tan\theta}$$

ϕ is the angle between the tangent to the equilibrium curve at O' and the x axis. Now

$$\frac{dy}{dx} = \frac{\alpha}{\{1+(\alpha-1)x\}^2}$$

and for $x = k_1$,

$$\tan \phi = \frac{\alpha}{\{1 + (\alpha - 1)k_1\}^2} = \frac{\alpha}{c^2},$$

where $c = 1 + (\alpha - 1)k_1$.

Also $\tan \theta = m$.

$$\therefore \quad \frac{\dfrac{x_0 - k_1}{k_2 - x_0}}{\dfrac{x_1 - k_1}{k_2 - x_1}} = \frac{\alpha}{mc^2} \qquad \ldots\ldots\ldots \quad (4a)$$

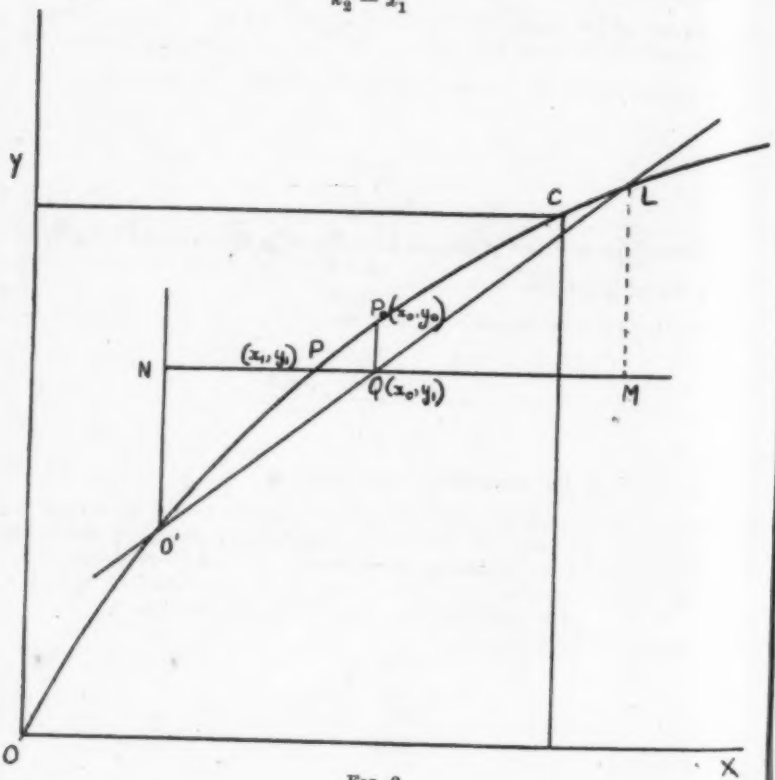

FIG. 2.

If x_0, x_1, x_2 . . . x_n represent compositions on successive plates in the column, then similarly

$$\frac{\dfrac{x_1 - k_1}{k_2 - x_1}}{\dfrac{x_2 - k_1}{k_2 - x_2}} = \frac{\dfrac{x_2 - k_1}{k_2 - x_2}}{\dfrac{x_3 - k_1}{k_2 - x_3}} = \ldots = \frac{\alpha}{mc^2}.$$

Therefore, by successive multiplication :

$$\frac{\dfrac{x_0 - k_1}{k_2 - x_0}}{\dfrac{x_n - k_1}{k_2 - x_n}} = \left(\frac{\alpha}{mc^2}\right)^n$$

or

$$\left(\frac{\alpha}{mc^2}\right)^n = \frac{(x_0 - k_1)(k_2 - x_n)}{(x_n - k_1)(k_2 - x_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which gives the number of theoretical plates required to pass from x_0 to x_n. For total reflux, $k_1 = 0$, $k_2 = 1$, $c = 1$ and $m = 1$ and equation (5) reduces to the well-known form. n becomes infinite when $x_n = k_1$ or $x_0 = k_2$, representing the intersection of the operating line with the equilibrium curve for a rectifying column or a stripping column respectively.

In the previous paper [1] the equation derived by Smoker [2] was converted into a form which may be written :

$$\left(\frac{\alpha}{mc^2}\right) = \frac{x_0''(1 - x_n'')}{x_n''(1 - x_0'')} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$x_0'' = \frac{x_0 - k_1}{k_2 - k_1} \quad \text{and} \quad x_n'' = \frac{x_n - k_1}{k_2 - k_1}.$$

Substituting these values in equation (6) then gives equation (5), which may also be written :

$$n \,.\, \log \frac{\alpha}{mc^2} = \log \left\{\frac{(x_0 - k_1)(k_2 - x_n)}{(x_n - k_1)(k_2 - x_0)}\right\} \quad . \quad . \quad . \quad . \quad (7)$$

This is a convenient form for computation. k_1 and k_2 must first be found either graphically by drawing the operating line and noting its intersections with the equilibrium curve, or analytically by solving for the abscissæ of the points of intersection from the equation :

$$mk + b = \frac{\alpha k}{1 + (\alpha - 1)k}$$

or

$$m(\alpha - 1)k^2 + \{m + b(\alpha - 1) - \alpha\}k + b = 0 \quad . \quad . \quad . \quad (8)$$

which is the equation originally given by Smoker.[2]

It should be noted that k_1 is the lesser root of equation (8) and k_2 is the greater root. An operating line for a rectifying column will give a value of k_1 between 0 and 1, while k_2 will be greater than 1. For a stripping column k_1 will be negative and k_2 will lie between 0 and 1. It should be noted that this convention is different from that used by Smoker, who does not use the root k_2, and denotes as k that root of equation (8) which lies between 0 and 1 for both a rectifying and a stripping column.

There is another simple proof of the relation given by equation (4a), which can be written in the form :

$$\frac{(x_0 - k_1)(k_2 - x_1)}{(x_1 - k_1)(k_2 - x_0)} = d,$$

where d is a constant. The relation between x_0 and x_1, as derived from the equilibrium curve and the operating line is:

$$mx_0 + b = \frac{\alpha x_1}{1 + (\alpha - 1)x_1}.$$

The constants k_1, k_2 and d can be chosen so that the two equations are identical. The two equations can be written:

$$x_1x_0(d - 1) + x_1(k_1 - dk_2) + x_0(k_2 - dk_1) + k_1k_2(d - 1) = 0$$

and $$x_1x_0m(\alpha - 1) + x_1\{b(\alpha - 1) - \alpha\} + mx_0 + b = 0.$$

The two are identical if

$$\frac{d - 1}{m(\alpha - 1)} = \frac{k_1 - dk_2}{b(\alpha - 1) - \alpha} = \frac{k_2 - dk_1}{m} = \frac{k_1k_2(d - 1)}{b}.$$

These relations give three equations for determining k_1, k_2, and d. From the first, second, and third relations it is seen that:

$$\frac{d - 1}{m(\alpha - 1)} = \frac{(k_1 + k_2)(1 - d)}{m + b(\alpha - 1) - \alpha},$$

so that $$-(k_1 + k_2) = \frac{m + b(\alpha - 1) - \alpha}{m(\alpha - 1)}.$$

Also $$k_1k_2 = \frac{b}{m(\alpha - 1)}.$$

Consequently k_1 and k_2 are the roots of equation (8).

Also $$(d - 1) = (\alpha - 1)(k_2 - dk_1).$$

$$\therefore \quad d = \frac{1 + (\alpha - 1)k_2}{1 + (\alpha - 1)k_1}.$$

Now

$$\begin{aligned}\{1 + (\alpha - 1)k_1\}\{1 + (\alpha - 1)k_2\} &= 1 + (\alpha - 1)(k_1 + k_2) + (\alpha - 1)^2k_1k_2 \\ &= 1 - \frac{\{m + b(\alpha - 1) - \alpha\}}{m} + \frac{b(\alpha - 1)}{m} \\ &= \frac{\alpha}{m}.\end{aligned}$$

Thus $$d = \frac{\alpha}{m\{1 + (\alpha - 1)k_1\}^2} = \frac{\alpha}{mc^2}.$$

Although equation (5) or (7) is simple in form, its application to separations where the top or bottom product contains only a small amount of one of the components necessitates a high degree of accuracy in computation. Usually, for a rectifying column, $x_0 = x_D$ and $x_n = x_F$, and for a stripping column, $x_0 = x_D$ and $x_n = x_W$. When the top product contains only a small amount of the heavier component, the point L is close to the point C in Fig. 2 and k_2 is very nearly equal to 1. Also x_0 is very nearly equal to 1, so that the term $(k_2 - x_0)$ in equation (7) is the difference of two nearly equal quantities, which must therefore be computed with a high

degree of accuracy to avoid excessive error in the difference. Similarly, for a stripping column producing a bottom product containing a small amount of the lighter component, the point O' will be close to O. k_1 will be small (and negative), and x_n will also be small, so that the term $(x_n - k_1)$ will be small. Also for reflux ratios close to the minimum reflux, it will be clear that, for a rectifying column, the term $(x_n - k_1)$ may be small, while for a stripping column the term $(k_2 - x_0)$ may be small. Exactly the same practical difficulty in computation arises if use is made of equation (6) or of the equation originally given by Smoker [2], namely :

$$\left(\frac{\alpha}{mc^2}\right)^n = \frac{x'_0\left\{1 - \frac{mc(\alpha - 1) \cdot x'_n}{\alpha - mc^2}\right\}}{x'_n\left\{1 - \frac{mc(\alpha - 1) \cdot x'_0}{\alpha - mc^2}\right\}} \quad . \quad . \quad . \quad . \quad (9)$$

where $x' = x - k_1$.

The difficulty also arises when a graphical method such as that of McCabe and Thiele [3] is used, and necessitates drawing on a large scale those parts of the diagram where the points representing plates are close together. The nomograph published by Bisesi [4] will also give insufficiently accurate results unless constructed on a large scale.

For example, when a mixture of two components with relative volatility 2·5 is fractionated with a reflux ratio of 3 to give a top product of composition $x_D = 0{\cdot}99$, the value of k_2 is 1·0071 and the difference $k_2 - x_D = k_2 - x_n = 0{\cdot}0171$. For three significant figures in the difference, five significant figures are required for the value of k_2.

The particular cases of a top product containing only a small amount of heavy component and a bottom product containing only a small amount of light component are of frequent occurrence in practical problems. For these cases simplified approximate equations can be derived which give results of satisfactory accuracy with less laborious computation than the exact equations (7) or (9). Thomson and Beatty [5] have made a careful study of various methods of calculating the number of theoretical plates for such conditions. They have shown that, by assuming the equilibrium curve to be linear near the ends of the x, y diagram, reasonably accurate results are obtained so long as the calculation is limited to moderate concentration ranges in these regions. For other cases, where there is a wide range between the feed concentration and the top or bottom product concentration, they do not recommend the use of that method. The simplified equations derived in the following are applicable to these conditions.

Number of Theoretical Plates—Rectifying Column.

Put $x_0 = x_D = 1 - \delta$, where δ is a small quantity.

Now $$m = \frac{R}{R+1} \quad \text{and} \quad b = \frac{x_D}{R+1} = (1 - m)(1 - \delta).$$

Substituting this value of b in equation (8) gives :

$$m(\alpha - 1)k^2 + \{2m - m\alpha - 1 - (\alpha - 1)(1 - m)\delta\}k + (1 - m)(1 - \delta) = 0 \quad . \quad . \quad (10)$$

Solving this equation, neglecting powers of δ higher than the first, gives:

$$k_2 = 1 + \frac{\alpha(1-m)\delta}{m\alpha - 1} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$k_1 = \frac{1-m}{m(\alpha-1)} - \frac{(1-m)\delta}{m(m\alpha-1)} = \frac{1-m}{m(\alpha-1)}\left\{1 - \frac{(\alpha-1)\delta}{m\alpha-1}\right\} . \quad . \quad (12)$$

Also $$k_2 - x_0 = k_2 - 1 + \delta = \frac{(\alpha-1)\delta}{m\alpha-1} \quad . \quad . \quad . \quad . \quad (13)$$

which gives the small term $(k_2 - x_0)$ in equation (7) with satisfactory accuracy by a slide-rule calculation.

Equation (10) can also be readily solved by noting that $k = 1$ is an approximate solution, since it is satisfied by $k = 1$ when $\delta = 0$. A second approximation to a solution is obtained by putting $k = 1 + \psi$, where ψ is small, and neglecting small quantities of the second order, which gives:

$$\psi = \frac{\alpha(1-m)\delta}{m\alpha-1} \text{ and } k_2 = 1 + \frac{\alpha(1-m)\delta}{m\alpha-1} \text{ as before.}$$

Also, since k_1 and k_2 are the roots of equation (10),

$$k_1 k_2 = \frac{(1-m)(1-\delta)}{m(\alpha-1)}$$

and $$k_1 = \frac{(1-m)(1-\delta-\psi)}{m(\alpha-1)} = \frac{1-m}{m(\alpha-1)}\left\{1 - \frac{(\alpha-1)\delta}{m\alpha-1}\right\} \text{ as before.}$$

Of the four terms on the right-hand side of equation (7), $(k_2 - x_0)$ or $(k_2 - x_D)$ is given by equation (13). Also $x_n - k_1 = x_F - k_1$ (where x_F is the feed composition) and is obtained from equation (12). If the feed is not composed of liquid at its boiling point, x_F should really be replaced by

$$\frac{(R+1)x_F + (q-1)x_D}{R+q},$$

where q is the heat required to vaporize 1 mol of feed divided by the molal heat of vaporization. In many cases this will be an unnecessary refinement unless q is quite small.

The term $(x_0 - k_1)$ is equal to $(x_D - k_1)$ and the term $(k_2 - x_n)$ is equal to $(k_2 - x_F)$.

It may be noted that

$$x_D - k_1 = 1 - \delta - k_1 = \frac{m\alpha - 1}{m(\alpha-1)} - \frac{(m^2\alpha - 1)\delta}{m(m\alpha-1)} \quad . \quad . \quad (14)$$

In many cases no substantial error will be involved if the second term containing δ is neglected.

Also $$k_2 - x_F = 1 - x_F + \frac{\alpha(1-m)\delta}{m\alpha-1} \quad . \quad . \quad . \quad . \quad (15)$$

and in many cases the term involving δ can be neglected.

An approximate value of $\frac{\alpha}{mc^2}$ can be obtained to facilitate calculation.

$$\frac{\alpha}{mc^2} = \frac{\alpha}{m\{1 + (\alpha - 1)k_1\}^2} = m\alpha\left\{1 + \frac{2(1 - m)(\alpha - 1)\delta}{m\alpha - 1}\right\} \quad . \quad . \quad (16)$$

Here again the term involving δ will be negligible in many cases. It will be found that the use of equations (11) to (16) greatly facilitates numerical computation and avoids the use of five-figure logarithms which are generally necessary when using equations (6), (7), or (9).

From the value of $(k_2 - x_0)$ given by equation (13), it will be seen by substituting it in equation (7) that n is approximately a linear function of $\log \delta$ when m and α are constant.

A comparison of the results given by the exact and the approximate methods is shown in Table I for various reflux ratios and top-product compositions, with $\alpha = 2{\cdot}5$ and $x_F = 0{\cdot}4$. It will be seen that the agreement is very satisfactory.

A less accurate equation can be obtained by neglecting the terms involving δ in equations (12), (14), (15), and (16), giving, by substitution in equation (7):

$$n \,.\, \log m\alpha = \log\left[\frac{(m\alpha - 1)^2(1 - x_F)}{m(\alpha - 1)^2\left\{x_F - \frac{(1 - m)}{m(\alpha - 1)}\right\}\delta}\right] \quad . \quad . \quad (17)$$

This equation will give substantial errors, of the order of perhaps 20 per cent., when used for reflux ratios near the minimum, mainly due to the error in the term $(x_F - k_1)$. It may, however, be useful for certain rough calculations.

Number of Theoretical Plates—Stripping Column.

In this case x_W is small and will be denoted by ϵ.

Since $$m = \frac{RP + qF}{RP + qF - W} \quad \text{and} \quad b = \frac{-Wx_W}{RP + qF - W}.$$

$$\therefore \qquad b = (1 - m)x_W = (1 - m)\epsilon.$$

Equation (8) then becomes:

$$m(\alpha - 1)k^2 + \{m + (\alpha - 1)(1 - m)\epsilon - \alpha\}k + (1 - m)\epsilon = 0 \quad . \quad (18)$$

When $\epsilon = 0$, one root of the equation is equal to zero, and therefore k_1 is small. Neglecting small terms of the second order in equation (18) gives:

$$k_1 = \frac{(1 - m)\epsilon}{\alpha - m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Since $$k_1k_2 = \frac{(1 - m)\epsilon}{m(\alpha - 1)},$$

$$\therefore \qquad k_2 = \frac{\alpha - m}{m(\alpha - 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

A second approximation for k_2 is obtained by putting

$$k_2 = \frac{\alpha - m}{m(\alpha - 1)} + \psi$$

where ψ is small. Substituting in equation (18) and neglecting small terms of the second order gives:

$$k_2 = \frac{\alpha - m}{m(\alpha - 1)} - \frac{\alpha(1 - m)\varepsilon}{m(\alpha - m)} = \frac{\alpha - m}{m(\alpha - 1)}\left\{1 - \frac{\alpha(1 - m)(\alpha - 1)\varepsilon}{(\alpha - m)^2}\right\} \quad . \quad (21)$$

The values of k_1 and k_2 given by equations (19) and (21) can also be obtained by solving equation (18) in the usual way and neglecting small terms of the second order.

The approximation for $\frac{\alpha}{mc^2}$ is:

$$\frac{\alpha}{mc^2} = \frac{\alpha}{m}\left\{1 - \frac{2(\alpha - 1)(1 - m)\varepsilon}{\alpha - m}\right\} \quad . \quad . \quad . \quad . \quad (22)$$

Also

$$x_n - k_1 = \varepsilon - k_1 = \frac{(\alpha - 1)\varepsilon}{\alpha - m} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Equations (19), (21), (22), and (23) are then used for computation of equation (7).

A comparison of the exact and approximate methods is given in Table II. As before, $\alpha = 2{\cdot}5$ and $x_F = 0{\cdot}4$. The results are given for various values of S, where S is defined by the operating line for a stripping column:

$$(S + 1)x = Sy + x_W \text{ and } m = \frac{S + 1}{S}.$$

For a stripping column on which a rectifying column is superimposed:

$$S = \frac{RP + qF - W}{W} = \frac{(R + 1)x_F - (R + q)x_W - (1 - q)x_D}{x_D - x_F}$$

As previously pointed out by the author,[6] the quantity S may be termed the "revaporization ratio." It represents the number of mols of vapour returned by the reboiler to the stripping column per mol of bottom product withdrawn. It is thus exactly analogous to the reflux ratio in a rectifying column which represents the number of mols of condensate returned by the condenser to the rectifying column per mol of top product withdrawn. As a more convenient name for the quantity S, "reboil ratio" is suggested.

It will be seen from Table II that the agreement between the exact and the approximate methods is very satisfactory.

When equation (7) is used for a rectifying column, putting $x_0 = x_D$ and $x_n = x_F$, the value of n obtained is the number of plates in the rectifying column, including the feed-plate. For a rectifying column used alone, mounted on a still pot, the pot would be included as a plate instead of the feed-plate in the value of n. When equation (7) is used for a stripping column, putting $x_0 = x_F$ and $x_n = x_W$, the value of n obtained is the number of plates in the stripping column below the feed-plate and includes the still pot counted as one plate. For the common case of a rectifying column

superimposed on a stripping column the total number of actual plates will be the sum of the two values of n less one, the still pot being excluded.

When α is not quite constant, it will usually be desirable to follow the suggestion of Thomson and Beatty [5] and use the value of α corresponding to the region of the equilibrium curve where the plates are closest together. This will usually be at one of the ends of the equilibrium curve.

A less accurate equation for the stripping column can be derived by using the value of k_2 given by equation (20) and neglecting ε in equation (22) and noting that:

$$x_0 - k_1 = x_F - k_1 = x_F \text{ approximately}$$

and

$$k_2 - x_n = k_2 - \varepsilon = k_2 \text{ approximately.}$$

Then

$$n \cdot \log \frac{\alpha}{m} = \log \left[\frac{(\alpha - m)^2 x_F}{m(\alpha - 1)^2 \left\{ \frac{\alpha - m}{m(\alpha - 1)} - x_F \right\} \varepsilon} \right] \quad . \quad . \quad (24)$$

This equation is subject to the same limitations that were pointed out in connection with equation (17).

Number of Transfer Units.

It has previously been shown [1] that the number of transfer units is given by the equation:

$$N_{OG} = \frac{1}{\beta - 1} \left[\log_e \frac{x_0''}{x_n''} + \beta \cdot \log_e \left\{ \frac{1 - x_n''}{1 - x_0''} \right\} \right] . \quad . \quad . \quad (25)$$

where

$$\beta = \frac{\alpha}{mc^2} \text{ and } x'' = \frac{x - k_1}{k_2 - k_1}.$$

Therefore

$$N_{OG} = \frac{1}{\frac{\alpha}{mc^2} - 1} \left[\log_e \left\{ \frac{x_0 - k_1}{x_n - k_1} \right\} + \frac{\alpha}{mc^2} \cdot \log_e \left\{ \frac{k_2 - x_n}{k_2 - x_0} \right\} \right] . \quad . \quad (26)$$

The equations previously derived for k_1, k_2, etc., can be used for the computation of equation (26) exactly as for equation (7).

Minimum Reflux Ratio and Minimum Number of Plates—Rectifying Column.

The minimum reflux ratio, R_0, is given by

$$R_0 = \frac{x_D - y_F}{y_F - x_F},$$

which reduces to

$$R_0 = \frac{1}{(\alpha - 1)x_F} - \frac{\delta\{1 + (\alpha - 1)x_F\}}{x_F(1 - x_F)(\alpha - 1)} \quad . \quad . \quad . \quad (27)$$

As a first approximation, which is sufficient for most purposes

$$R_0 = \frac{1}{(\alpha - 1)x_F} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The minimum reflux operating line with slope $m_0 = \frac{R_0}{R_0 + 1}$ intersects the equilibrium curve at $x = x_F$, which is the corresponding value of k_1. Then, from equation (12):

$$x_F = \frac{1 - m_0}{m_0(\alpha - 1)} - \frac{(1 - m_0)\delta}{m_0(m_0\alpha - 1)} \quad . \quad . \quad . \quad . \quad (29)$$

and

$$x_F - k_1 = \frac{1 - m_0}{m_0(\alpha - 1)} - \frac{1 - m}{m(\alpha - 1)} - \delta\left\{\frac{1 - m_0}{m_0(m_0\alpha - 1)} - \frac{1 - m}{m(m\alpha - 1)}\right\}$$

$$= \frac{1 - m_0}{m_0(\alpha - 1)} - \frac{1 - m}{m(\alpha - 1)} \text{ approx.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

From equations (11) and (29):

$$k_2 - x_F = \frac{m_0\alpha - 1}{m_0(\alpha - 1)} + \delta\left\{\frac{\alpha(1 - m)}{m\alpha - 1} + \frac{1 - m_0}{m_0(m_0\alpha - 1)}\right\}$$

$$= \frac{m_0\alpha - 1}{m_0(\alpha - 1)} \text{ approx.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Also, from equation (12):

$$x_D - k_1 = \frac{m\alpha - 1}{m(\alpha - 1)} - \frac{(m^2\alpha - 1)\delta}{m(m\alpha - 1)}$$

$$= \frac{m\alpha - 1}{m(\alpha - 1)} \text{ approx.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Then, substituting from equations (30), (31), (32), and (13) in equation (5) gives:

$$\left(\frac{\alpha}{mc^2}\right)^n = \frac{(m\alpha - 1)^2(m_0\alpha - 1)}{(m - m_0)(\alpha - 1)^2\delta} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

For total reflux, the minimum number of plates, n_0, is given by

$$\alpha^{n_0} = \frac{x_D(1 - x_F)}{x_F(1 - x_D)} = \frac{1 - x_F}{x_F \cdot \delta}$$

or

$$\alpha^{n_0} = \frac{(m_0\alpha - 1)}{(1 - m_0)\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

From equations (33) and (34):

$$\frac{\left(\frac{\alpha}{mc^2}\right)^n}{\alpha^{n_0}} = \frac{(m\alpha - 1)^2(1 - m_0)}{(m - m_0)(\alpha - 1)^2} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

As an approximation from equation (16),

$$\frac{\alpha}{mc^2} = m\alpha.$$

Therefore

$$\frac{(m\alpha)^n}{\alpha^{n_0}} = \frac{(m\alpha - 1)^2(1 - m_0)}{(m - m_0)(\alpha - 1)^2} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

This equation can be used for plotting a curve showing the variation of n with m or R.

Minimum Reboil Ratio and Minimum Number of Plates—Stripping Column.

As pointed out earlier in this paper, the slope, m_0, of the operating line for the minimum reboil ratio, S_0, is given by

$$m_0 = \frac{S_0 + 1}{S_0} = \frac{y_F - x_W}{x_F - x_W}$$

and

$$S_0 = \frac{x_F - x_W}{y_F - x_F}$$

$$\therefore \quad S_0 = \frac{1 + (\alpha - 1)x_F}{(\alpha - 1)(1 - x_F)}\left(1 - \frac{\varepsilon}{x_F}\right) = \frac{1 + (\alpha - 1)x_F}{(\alpha - 1)(1 - x_F)} \text{ approx.} \quad . \quad (37)$$

Noting that x_F is the value of k_2 when $m = m_0$, the following approximate equations can be derived by the same procedure used for the rectifying column:

$$x_F = \frac{\alpha - m_0}{m_0(\alpha - 1)} - \frac{\alpha(1 - m_0)\varepsilon}{m_0(\alpha - m_0)} \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$$x_F - k_1 = \frac{\alpha - m_0}{m_0(\alpha - 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

$$k_2 - x_F = \frac{\alpha - m}{m(\alpha - 1)} - \frac{\alpha - m_0}{m_0(\alpha - 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$k_2 - x_W = \frac{\alpha - m}{m(\alpha - 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Substituting in equation (5) from these equations and equation (23):

$$\left(\frac{\alpha}{mc^2}\right)^n = \frac{(\alpha - m_0)(\alpha - m)^2}{\alpha(\alpha - 1)^2(m_0 - m)\varepsilon} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

For total reflux,

$$\alpha^{n_0} = \frac{x_F(1 - x_W)}{x_W(1 - x_F)} = \frac{x_F}{(1 - x_F)\varepsilon} \text{ approx.}$$

or

$$\alpha^{n_0} = \frac{\alpha - m_0}{\alpha(m_0 - 1)\varepsilon} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Therefore

$$\frac{\left(\frac{\alpha}{mc^2}\right)^n}{\alpha^{n_0}} = \frac{(\alpha - m)^2(m_0 - 1)}{(\alpha - 1)^2(m_0 - m)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

As an approximation from equation (22), $\frac{\alpha}{mc^2} = \frac{\alpha}{m}$.

Then

$$\frac{\left(\frac{\alpha}{m}\right)^n}{\alpha^{n_0}} = \frac{(\alpha - m)^2(m_0 - 1)}{(\alpha - 1)^2(m_0 - m)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Reflux Ratio and Reboil Ratio.

It has been pointed out that there is a close analogy between reflux ratio for a rectifying column and reboil ratio for a stripping column. It can

further be shown that, by suitable transformation, the calculation of plates for a stripping column can be made by using methods of calculation relating to a rectifying column. Fig. 3 shows an operating line for a stripping column, which cuts the equilibrium curve at D and F and the diagonal OB at E ($x = x_W$). Its inclination to the x axis is given by $m = \tan\theta = \frac{S+1}{S}$. If Fig. 3 is rotated through 180° about the diagonal

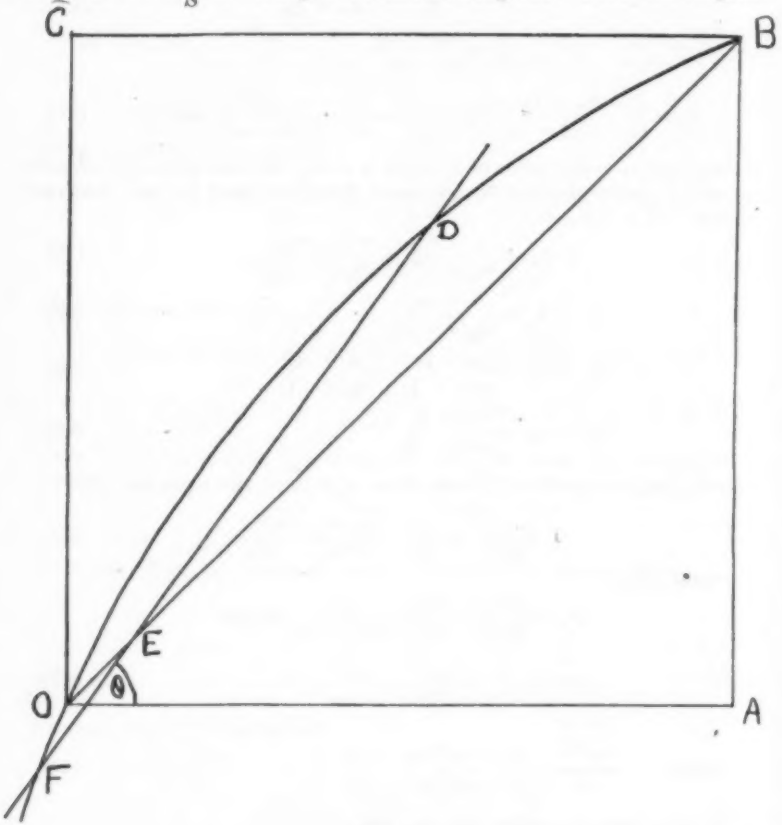

FIG. 3.

AC, the result is Fig. 4. The equilibrium curve is unchanged since it is symmetrical with respect to a line joining A and C. The stripping-column line DEF of Fig. 3 has become a rectifying-column line in Fig. 4. It now has an inclination of $\left(\frac{\pi}{2} - \theta\right)$ to the horizontal axis and its slope is

$$\tan\left(\frac{\pi}{2} - \theta\right) = \cot\theta = \frac{S}{S+1}$$

Taking B as the new origin in Fig. 4, the co-ordinates of the point E are $(1 - x_W)$. If x' and y' are the new co-ordinates in Fig. 4, the equation of the line DEF is

$$y' = \frac{S}{S+1} \cdot x' + \frac{1 - x_W}{S+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

This now represents an operating line for a rectifying column with a reflux ratio S and a top product $(1 - x_W)$. The calculation of plates for a stripping

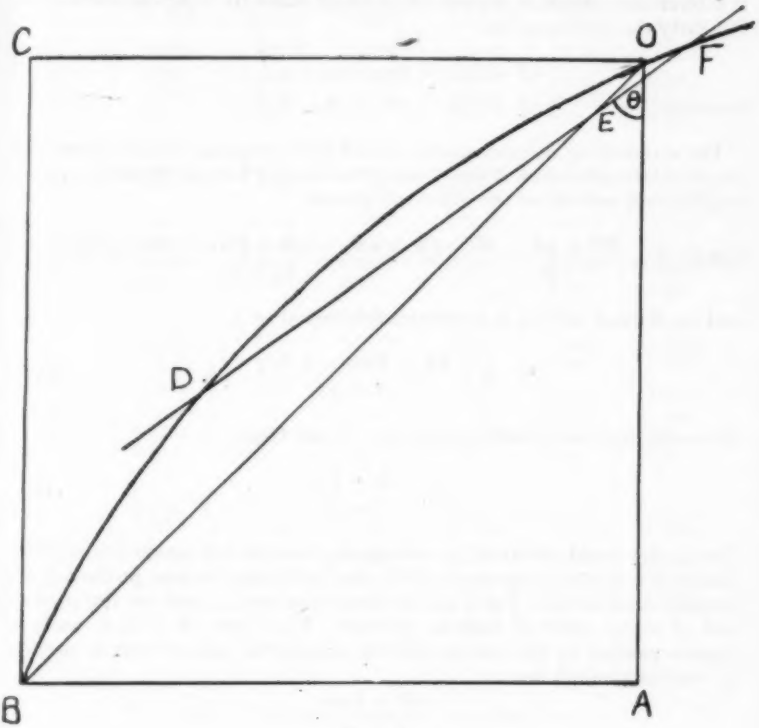

FIG. 4.

column can therefore be carried out by using the same equations as for a rectifying column, using S instead of R and $(1 - x_W)$ instead of x_D. It should be noted that if x_F is the feed composition for the stripping column in Fig. 3, the corresponding feed composition for the rectifying column in Fig. 4 is $(1 - y_F) = x'_F$.

The above results can also be demonstrated analytically. The relation between the (x, y) system of co-ordinates of Fig. 3 and the (x', y') system of co-ordinates of Fig. 4 is

$$x = 1 - y' \text{ and } y = 1 - x' \quad . \quad . \quad . \quad . \quad . \quad (47)$$

These equations indicate that the mol fraction of the lighter component in the liquid at any point in Fig. 3 becomes the mol fraction of the heavier component in the vapour at the corresponding point in Fig. 4. Writing the equilibrium curve in the form

$$\frac{y}{1-y} = \frac{\alpha x}{1-x}$$

it is obviously identical in form when transformed by using equations (47). Similarly the operating line

$$(S+1)x = Sy + x_W$$

becomes

$$(S+1)y' = Sx' + (1 - x_W).$$

For a rectifying column superimposed on a stripping column there is a simple relation between R and S when the top and bottom products contain only a small amount of the other component.

Since $$S = \frac{RP + qF - W}{W} = \frac{(R+1)x_F - (R+q)x_W - (1-q)x_D}{x_D - x_F}$$

and x_W is small and x_D is approximately equal to 1,

$$\therefore \qquad S = \frac{(R+1)x_F - 1 + q}{1 - x_F} \qquad \ldots\ldots \quad (48)$$

When the feed is at boiling-point, $q = 1$ and then

$$S = \frac{(R+1)x_F}{1 - x_F} \qquad \ldots\ldots \quad (49)$$

This is also readily derived by considering that the top product is approximately the lighter component of the feed while the bottom product is the heavier component. For 1 mol of feed there are x_F mols of top product and $(1 - x_F)$ mols of bottom product. There are $(R+1)\,x_F$ mols of vapour passing up the column and the number of mols of vapour per mol of bottom product are

$$\frac{(R+1)x_F}{1 - x_F}$$

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Rectifying Column—Summary of Results.

	$x_D = 0{\cdot}99$.		$x_D = 0{\cdot}97$.		$x_D = 0{\cdot}95$.	
	Appr.	Exact.	Appr.	Exact.	Appr.	Exact.
			$R = 1{\cdot}8$.			
k_1 . .	0·361	0·3614	0·343	0·3447	0·324	0·3291
k_2 . .	1·0147	1·0145	1·0441	1·0424	1·0735	1·0691
$\frac{a}{mc^2}$ . .	1·6354	1·6353	1·6922	1·6898	1·7490	1·7431
$(x_p - k_1)$.	0·039	0·0386	0·057	0·0553	0·076	0·0709
$(k_2 - x_D)$.	0·0247	0·0245	0·0741	0·0724	0·1235	0·1191
n . .	12·20	12·23	8·70	8·75	6·85	6·89
			$R = 2$.			
k_1 . .	0·3258	0·3259	0·3108	0·3120	0·2958	0·2989
k_2 . .	1·0125	1·0124	1·0375	1·0364	1·0625	1·0595
$\frac{a}{mc^2}$ . .	1·6917	1·6916	1·7417	1·7401	1·7917	1·7875
$(x_p - k_1)$.	0·0742	0·0741	0·0892	0·0880	0·1042	0·1011
$(k_2 - x_D)$.	0·0225	0·0224	0·0675	0·0664	0·1125	0·1095
n . .	10·45	10·46	7·65	7·72	6·19	6·29
			$R = 3$.			
k_1 . .	0·2184	0·2184	0·2108	0·2111	0·2032	0·2040
k_2 . .	1·0071	1·0071	1·0214	1·0211	1·0357	1·0349
$\frac{a}{mc^2}$ . .	1·8911	1·8912	1·9232	1·9226	1·9558	1·9543
$(x_p - k_1)$.	0·1816	0·1816	0·1892	0·1888	0·1968	0·1960
$(k_2 - x_D)$.	0·0171	0·0171	0·0514	0·0511	0·0857	0·0849
n . .	7·87	7·87	5·93	5·94	4·98	5·00
			$R = 4$.			
k_1 . .	0·1642	0·1642	0·1592	0·1593	0·1542	0·1545
k_2 . .	1·0050	1·00499	1·0150	1·01488	1·0250	1·02464
$\frac{a}{mc^2}$ . .	2·1020	2·0119	2·0360	2·0357	2·0600	2·0595
$(x_p - k_1)$.	0·2358	0·2358	0·2408	0·2407	0·2458	0·2455
$(k_2 - x_D)$.	0·0150	0·01499	0·0450	0·04488	0·075	0·07464
n . .	7·08	7·08	5·39	5·39	4·56	4·57

Stripping Column—Summary of Results.

	$x_W = 0{\cdot}01$.		$x_W = 0{\cdot}03$.		$x_W = 0{\cdot}05$.	
	Appr.	Exact	Appr.	Exact.	Appr.	Exact.
			$S = 2$.			
k_1 . .	−0·005	−0·00491	−0·015	−0·01423	−0·025	−0·02296
k_2 . .	0·4527	0·4527	0·4694	0·4687	0·4861	0·4841
$\frac{a}{mc^2}$ . .	1·6917	1·6916	1·7417	1·7402	1·7917	1·7840
$(k_2 - x_p)$.	0·0527	0·05269	0·0694	0·06867	0·0861	0·08407
$(x_W - k_1)$.	0·015	0·01491	0·045	0·04423	0·075	0·07296
n . .	10·31	10·32	7·33	7·39	5·75	5·87

STRIPPING COLUMN—SUMMARY OF RESULTS (*contd.*).

	$x_W = 0{\cdot}01$.		$x_W = 0{\cdot}03$.		$x_W = 0{\cdot}05$.	
	Appr.	Exact.	Appr.	Exact.	Appr.	Exact.
			$S = 3$.			
k_1 . .	−0·002857	−0·002836	−0·008571	−0·008349	−0·01429	−0·01368
k_2 . .	0·5887	0·5887	0·5994	0·5992	0·6101	0·6095
$\frac{a}{mc^3}$ . .	1·8911	1·8910	1·9232	1·9230	1·9554	1·9545
$(k_2 - x_F)$.	0·1887	0·1887	0·1994	0·1992	0·2101	0·2095
$(x_W - k_1)$.	0·01286	0·01284	0·03857	0·03835	0·06429	0·06368
n . .	7·17	7·17	5·22	5·22	4·24	4·24
			$S = 4$.			
k_1 . .	−0·002	−0·001991	−0·006	−0·005897	−0·010	−0·009714
k_2 . .	0·6707	0·6707	0·6787	0·6786	0·6867	0·6864
$\frac{a}{mc^3}$ . .	2·012	2·0120	2·036	2·0359	2·060	2·0595
$(k_2 - x_F)$.	0·2707	0·2707	0·2787	0·2786	0·2867	0·2864
$(x_W - k_1)$.	0·012	0·01199	0·036	0·03590	0·060	0·05971
n . .	6·30	6·30	4·59	4·60	3·76	3·76

OBITUARY.

MR. HIRAM J. HALLE.

HIRAM J. HALLE, President of Universal Oil Products Company, died on 29th May at his home, Pound Ridge, New York. His health had been failing for some time.

Mr. Halle was born in Cleveland, Ohio, seventy-seven years ago. He entered petroleum refining at the time the automobile was coming into mass production, and for more than twenty-five years was an outstanding figure in the growth and development of the refining industry.

He became president of U.O.P. in 1915, and under his leadership, the Universal organization took an important part in the invention, development and servicing of processes which have revolutionized the refining industry, starting with the Dubbs cracking process and progressing through continuous research and development work to the perfecting of a number of catalytic refining processes.

CORRIGENDUM.

JULY JOURNAL.

"The Correlation of Cetane Number with other Physical Properties of Diesel Fuels."

P. 196. Table 1. Column 3. Delete "Outside" before $\pm$ 5.

P. 197. Delete "(7)" before equation.